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(54) OXIDATION RESISTANT MOLYBDENUM ALLOY

OXIDATIONSBESTÄNDIGE MOLYBDÄNLEGIERUNG

ALLIAGE DE MOLYBDENE RESISTANT A L'OXYDATION

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- **Proc. 4th Int. Conf. on Rapidly Solidified Quenced Materials, Sendai,1981, p. 1245-1248**

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to molybdenum alloys that have been made oxidation resistant by the addition of silicon and boron.

2. Related Art

[0002] Molybdenum metal is an attractive material for use in jet engines and other high temperature applications because it exhibits excellent strength at high temperature. In practice, however the utility of molybdenum has been limited by its susceptibility to oxidation. When molybdenum or molybdenum alloys are exposed to oxygen at temperatures in excess of about 540°C (1000°F), the molybdenum is oxidized to molybdenum trioxide and vapourised from the surface: resulting in shrinkage and eventually disintegration of the molybdenum or molybdenum alloy article. Most previously disclosed methods of preventing oxidation of molybdenum at high temperature in oxidizing environments (such as air) have required a coating to be applied to the molybdenum alloy. Applied coatings are sometimes undesirable due to factors such as: poor adhesion, the need for extra manufacturing steps, and cost.
Furthermore, damage to the coating can result in rapid oxidation of the underlying molybdenum alloy. Thus, there is a need for molybdenum alloys which possess a combination of good strength and enhanced oxidation resistance at high temperature. There is a corresponding need for methods of making these alloys.
[0003] Inoue et al (in Proc 4th Int. Conf. on Rapidly Quenching Metals (Sendai 1981) pages 1245 to 1248) investigates the superconductive properties of Mo-Si-B ternary amorphous alloys obtained by melt quenching.

SUMMARY OF THE INVENTION

[0004] The invention is defined in the claims.
[0005] The molybdenum alloys of the present invention are composed of a matrix of body-centered cubic (BCC) molybdenum and dispersed intermetallic phase wherein the alloys comprise 10 to 70 volume % molybdenum borosilicide, less than 20 volume % molybdenum boride, and less than 20 volume % molybdenum silicide and consist of:

C	0.0-1.0%
Ti	0.0-15.0%
Hf	0.0-10.0%
Zr	0.0-10.0%
W	0.0-20.0%
Re	0.0-45.0%
Al	0.0-5.0%
Cr	0.0-5.0%
V	0.0-10.0%
Nb	0.0-2.0%
Ta	0.0-2.0%
B	0.5-4.0%
Si	1.0-4.5%

and one or more of Ti, Zr, Hf or Al in an amount of 0.3-10% and the balance is 50-98.5% Mo apart from impurities wherein % is weight %, the molybdenum alloy optionally comprising up to 2.5 volume % carbides.
[0006] Smaller amounts of silicon and boron will not provide adequate oxidation resistance: larger amounts will embrittle the alloys. All percentages (%) disclosed herein refer to weight percent unless otherwise specified. In the foregoing composition ranges, the molybdenum metal component contains one or more of the following elemental additions in replacement of an equivalent amount of molybdenum:

ELEMENT	RANGE IN WEIGHT % OF THE FINAL ALLOY	PREFERRED RANGE
C	0.01 to 1.0	0.03 to 0.3

(continued)

ELEMENT	RANGE IN WEIGHT % OF THE FINAL ALLOY	PREFERRED RANGE
Ti	0.1 to 15.0	0.3 to 10.0
Hf	0.1 to 10.0	0.3 to 3.0
Zr	0.1 to 10.0	0.3 to 3.0
W	0.1 to 20.0	0.3 to 3.0
Re	0.1 to 45.0	2.0 to 10.0
Al	0.1 to 5.0	0.5 to 2.0
Cr	0.1 to 5.0	0.5 to 2.0
V	0.1 to 10.0	0.3 to 5.0
Nb	0.1 to 2.0	0.3 to 1.0
Ta	0.1 to 2.0	0.3 to 1.0

[0007] When the alloys of the present invention are exposed to an oxidizing environment at temperatures greater than 540°C (1000°F), the material will produce a volatile molybdenum oxide in the same manner as conventional molybdenum alloys. Unlike conventional alloys, however, oxidation of alloys of the present invention produces build-up of a borosilicate layer at the metal surface that will eventually shut off the bulk flow of oxygen. For example, an X-ray map of a sample of the allow Mo-0.3%Hf-2.0%Si-1.0%B after oxidation in air at 1090°C (2000°C) for two hours showed a borosilicate layer about 10μm thick. This is shown in Figure 1. After a borosilicate layer is built up, oxidation is controlled by diffusion of oxygen through the borosilicate and will, therefore, proceed at a much slower rate.

[0008] Adding a reactive element such as titanium, zirconium, hafnium, and/or aluminium to the alloy (1) promotes wetting of the borosilicate layer once it has formed, (2) raises the melting point of the borosilicate, and (3) forms a more refractory oxide layer below the initial borosilicate layer further impending oxygen transport to the molybdenum matrix. The addition of such elements is particularly advantageous for alloys that are intended to be used at high temperatures (ie. about 1090°C (2000°F). In some embodiments, it is advantageous to add carbon to the alloy in order to produce small amounts (less than 2.5 volume %) of carbide to strengthen the alloy. The alloys of the present invention contain 10 to 70 volume % molybdenum borosilicide (Mo_5SiB_2), less than 20 volume % molybdenum boride (Mo_2B), and less than 20 volume % molybdenum silicide (Mo_5Si_3 and/or Mo_3Si). In a preferred embodiment, the alloys of the present invention comprise less than 2.5 volume % carbide and less than 3 volume % of non-BCC molybdenum phases, other than the carbide, silicide, and boride phases discussed above. Preferred alloys of the present invention are formulated to exhibit oxidation resistance such that articles composed of these alloys lose less than about 0.01" (about 0.25mm) in thickness after exposure to air for two hours at the maximum use temperature of the article. The maximum use temperature of these articles is typically between 820°C (1500°F) and 1370°C (2500°F). It is contemplated that the alloys of the present invention be formulated for the best overall combination of oxidation resistance and mechanical properties for each article's particular requirements.

[0009] The alloys of the present invention can be produced through a variety of methods including, but not limited to: powder processing (prealloyed powder, blended powder, blended elemental powder, etc.), and deposition (physical vapor deposition, chemical vapor deposition, etc.). Powders of the alloys of the present invention can be consolidated by methods including, but not limited to: extrusion, hot pressing, hot isostatic pressing, sintering, hot vacuum compaction, etc. After consolidation, the alloys can be thermal-mechanically processed by methods used conventionally on molybdenum alloys.

[0010] While the alloys of the present invention may be used in less demanding conditions, these alloys are particularly desirable for use in situations requiring both good strength and good oxidation resistance at temperatures in excess of 540°C (1000°F). Particular applications include, but are not limited to, jet engine parts such as turbine blades, vanes, seals, and combustors.

BRIEF DESCRIPTION OF THE FIGURES

[0011] Fig. 1 shows an X-ray map of borosilicate scale (white area) produced on the alloy Mo-0.3%Hf-2.0%Si-1.0%B by oxidation in air at 1090°C (2000°F) for two hours. The magnification is 1000X so that 1cm is equal to 10 microns.

[0012] Fig.2 shows the comparison of the oxidation resistance of an alloy of the present invention (Mo-6.0%Ti-2.2%Si-1.1%B) and a conventional (Mo-0.5%Ti-0.08%Zr-0.03%C, TZM) alloy molybdenum which have been exposed to air for two hours at 1370°C (2500°F) and 1090°C (2000°F), respectively.

DETAILED DESCRIPTION OF THE INVENTION

[0013] Alloys of the present invention are made by combining 10 to 70 volume % molybdenum borosilicide, less than 20 volume % molybdenum boride, and less than 20 volume % molybdenum silicide and consisting of:

C	0.0-1.0%
Ti	0.0-15.0%
Hf	0.0-10.0%
Zr	0.0-10.0%
W	0.0-20.0%
Re	0.0-45.0%
Al	0.0-5.0%
Cr	0.0-5.0%
V	0.0-10.0%
Nb	0.0-2.0%
Ta	0.0-2.0%
B	0.5-4.0%
Si	1.0-4.5%

and one or more of Ti, Zr, Hf or Al in an amount of' 0.3-10% and the balance is 50-98.5% Mo apart from impurities wherein % is weight %, the molybdenum alloy optionally comprising up to 2.5 volume % carbides.

[0014] The intermetallic phases of the alloy of the present invention are brittle. Therefore, in order to obtain ductile alloys, the material must be processed so that there is a matrix of ductile BCC molybdenum surrounding discrete particles of intermetallic phase. This structure is obtained, in preferable embodiments of the present invention by: 1) blending molybdenum powder with either a pre-alloyed intermetallic powder (such as molybdenum borosilicide) or boron and silicon powder, followed by consolidating the powder at a temperature below the melting temperature. The latter process is more expensive but it produces a material having a finer, more processable microstructure.

[0015] In order to obtain desired shape, strength and hardness, alloys of the present invention can be processed in the same manner as other high strength molybdenum alloys. Preferred alloys of the present invention can not be shaped by recasting and slow solidification since slow solidification forms excessively large dispersoids and, as a result embrittled alloys.

[0016] In the most preferable method of making alloys of the present invention, elemental molybdenum, silicon and boron, in the portions defined above, are combined in a melt. Alloy from the melt is rapidly solidified into a fine powder using an atomization device based on US Patent No. 4,207,040. The device from this patent was modified by the substitution of a bottom pour 250 kilowatt plasma arc melter for the induction heated crucible. The resultant powder is screened to minus 80 mesh. This powder is loaded into a molybdenum extrusion can and then evacuated. The material is then given a pre-extrusion heat treatment of 1760°C (3200°F) for 2 hours and then is extruded at a cross-sectional ratio of 6 to 1 at a temperature of 1510°C (2750°F). The extrusion is then swaged 50% in 5% increments at 1370°C (2500°F). The molybdenum can is then removed and the remaining material is then swaged down to the desired size at temperatures of 1260°C (2300°F) to 1370°C (2500°F). All heat treatments and preheating should be done in an inert atmosphere, in vacuo, or in hydrogen.

[0017] The use of titanium, zirconium, hafnium and/or aluminum in the alloys of the present invention promotes wetting of the metal surface by the oxide and increases the melting point of the oxide. Larger additions (ie. 0.3% to about 10%) of these elements creates a refractory oxide layer under the initial borosillicate layer. The addition of titanium is especially preferred for this use.

[0018] Because elements such as titanium, zirconium, hafnium and aluminum can have a small deleterious effect on oxidation resistance at temperatures below about 980°C (1800°F); the addition of these elements is undesirable for some low temperature applications.

[0019] The tensile strength of the alloys of the present invention are increased by the addition of solid solution strengthening agents. Additions of titanium, hafnium, zirconium, chromium, tungsten, vanadium and rhenium strengthen the molybdenum matrix. In addition to strengthening the material, rhenium lowers the ductile/brittle transition temperature of the BCC matrix.

[0020] Since titanium, zirconium, and hafnium are potent silicide and boride formers, these elements improve the mechanical properties of the alloys by increasing the fracture strength of the intermetallic phases. In some embodiments, the intermetallic phases are strengthened by the use of carbon as an alloying addition.

[0021] In certain, preferred embodiments, alloys of the present invention are additionally strengthened through solutioning and aging. In these alloys small amounts of silicon and/or carbon can be taken into solution in the BCC matrix by heating the alloy to over 1540°C (2800°F). A fine dispersion of either silicides or carbides can then be produced in the alloy by either controlled cooling of the material. or by cooling it fast enough to keep the silicon and/or carbon in solution and then precipitating silicides and/or carbides by aging the material between 1480°C (2700°F) and 1260°C (2300°F). Tungsten and rhenium decrease the solubility of silicon in the alloy and when added in small amounts (i.e. about 0.1-3.0%) improve the stability of any fine silicides present. In alloys with an insufficient amount of silicon present for an aging response, vanadium may be added to increase the solubility of silicon in the alloy. The elements titanium, zirconium, and hafnium may be added to improve the aging response by promoting the formation of alloy carbides. In a preferred embodiment, the silicide or carbide fine dispersion particles consist essentially of particles having diameters between 10nm and 1 micron. In a more preferred embodiment, these fine dispersion particles are spaced apart by 0.1 to 10 microns.

[0022] In preferred embodiments. alloys of the present invention are composed of long grains having an aspect ratio of greater than 6 to 1.

[0023] Phases in alloys of the present invention were characterized by scanning electron microscope - energy dispersive x-ray analysis (SEM-EDX) and x-ray back scattering. In alloys containing only molybdenum, silicon and boron, the stable phases are Mo_5SiB_2, Mo_2B, and Mo_3Si. Alloys containing more than about 2% of additive elements such as titanium, zirconium or hafnium may have alloyed Mo_5Si_3 present either in addition to or in place of Mo_3Si. In a preferred embodiment, the molybdenum boride, silicide and borosilicide dispersion particles consist essentially of particles having diameters between 10 microns and 250 microns.

OXIDATION RESISTANCE

[0024] A series of tests were conducted that demonstrated the molybdenum alloys of the present invention to have a far greater oxidation resistance than previously known molybdenum alloys. All of the tests were performed using small arc castings made in an inert atmosphere from metal powders. In a comparative test, TZM, a commercially available molybdenum alloy, lost approximately 0.063mm (2.5 mils) per minute in an air furnace at 1090°C (2000°F). In comparison, an alloy of the present invention, having the composition Mo-6.0%Ti-2.6%Si-1.1%B lost approximately 0.05mm (2 mils) in two hours in an air furnace at 1360°C (2500°F) and formed an oxide layer that would greatly retard further oxidation. The alloy samples resulting from the two hour comparative test are shown in Figure 2.

[0025] A set of oxidation tests were performed that demonstrated the effects of various amounts of silicon and boron in molybdenum. These tests were conducted in an air furnace at 1090°C (2000°F) for 1 hour and used identically prepared samples consistly only of molybdenum, silicon and boron. The results of this test are shown in Table 1.

Table 1.

Oxidation Rates of Various Molybdenum Alloys at 1090°C (2000°F).		
Si	B	oxidation rate (mils/min)
1.0	0.5	0.7
1.0	4.0	0.07
4.5	4.0	0.02
4.5	0.5	0.5
0.5	0.5	1.6
1.0	0	2.0
5.0	0	1.3
1.0	7.0	0.05
4.5	7.0	0.05

[0026] The oxidation rate of 0.018mm (0.7 mils) per minute is one third that of TZM and represents the practical limit for a material that could survive in a coated condition in a short time non-manrated jet engine application where the use time of the material would be on the order of 15 minutes. As shown from the test data, the addition of 0.5%B results in significantly better oxidation resistance than silicon alone. More importantly, the Mo-1.0%Si material did not form a protective oxide and the Mo-5.0%Si formed a voluminous, porous oxide with extremely poor adherence to the base metal. An alloy containing 0.5%B and only 0.5%Si exhibited intermittent formation of a non-protective oxide and twice the oxidation rate of the alloy containing 0.5%B and 1.0%Si. The materials containing excessive boron, Mo-1.0%Si-

7.0%B and Mo-4.5%Si-7.0%B, demonstrated good oxidation rates but produced highly liquid oxides which flowed over and attacked the material the specimens were placed on. The oxides would be subject to degradation by any flowing media such as air passing over the material and would be easily removed by physical contact.

[0027] In another set of tests approximately 200 alloy compositions were made up of small arc castings and tested for oxidation resistance. These oxidation tests were conducted at temperatures of 820°C (1500°F), 1090°C (2000°F) and 1370°C (2500°F). The tests were done for 2 hours in an air furnace. The specimens were rectangles approximately 1\4 x 3\8 x 3\4 inches long. It was found that as the amount of silicon and boron increased, the amount of intermetallic present also increased, and the better the oxidation became. However, increasing amounts of silicon and boron also made the material difficult to process for useful mechanical properties. At 2% silicon and 1% boron there is approximately 30 to 35 volume % intermetallic in the material. Additions of titanium, zirconium and hafnium improve the oxidation resistance of the material at 2000°F without causing an increase in the amount of intermetallic. These elements caused a slight but acceptable decrease in the oxidation resistance at 820°C (1500°F). They caused a significant increase in the oxidation resistance at 1370°C (2500°F).

[0028] The following compositions are examples of alloys that were found to be highly oxidation resistant at 1500, 2000. and 1360°C (2500°F): Mo-2.0%Ti-2.0%Si-1.0%B; Mo-2.0%Ti-2.0%Si-1.0%B-0.25%Al; Mo-8.0%Ti-2.0%Si-1.0%B; Mo-0.3%Hf-2.0%Si-1.0%B; Mo-1.0%Hf-2.0%Si-1.0%B; Mo-0.2%Zr-2.0%Si-1.0%B; and Mo-6.0%Ti-2.2%Si-1.1%B. Mo-6.0%Ti-2.2%Si-1.1%B showed particularly excellent oxidation resistance at 1090°C (2000°F) and 1370°C (2500°F).

STRENGTH

[0029] The tensile properties of Mo-0.3%Hf-2.0%Si-1.0%B are shown in Table 2. The alloy used in testing was prepared by rapid solidification from the melt followed by extrusion as described above with reference to the most preferred embodiment. Tensile strength testing was conducted on bars 0.38cm (0.152") in diameter, 2.5cm (1") long with threaded grips and 0.63cm (0.25") radius shoulders. For comparison, the yield strength of TZM at 1090°C (2000°F) is 70 ksi and the yield strength of a single crystal nickel superalloy at 1090°C (2000°F) is 40 ksi. For a review of molybdenum alloys and their strengths; see J.A. Shields. "Molybdenum and Its Alloys," Advanced Materials & Processes, pp. 28-36, Oct. 1992.

Table 2.

Tensile Properties of Mo-.3%Hf - 2%Si - 1% B.				
Temperature	Yield Strength	Ultimate Strength	%El	%RA
RT	115.3	115.7	.2	0
1000°F	112.5	140.2	2.5	0.8
1500°F	103.4	148.0	2.6	1.6
2000°F	68.4	77.0	21.5	29.4
2300°F	36.3	43.3	28.2	36.0
2500°F	24.6	29.5	31.6	39.8

Claims

1. A molybdenum alloy composed of a matrix of body centred cubic molybdenum and dispersed intermetallic phases comprising 10 to 70 volume % molybdenum borosilicide, less than 20 volume % molybdenum boride, and less than 20 volume % molybdenum silicide and consisting of:

C	0.0-1.0%
Ti	0.0-15.0%
Hf	0.0-10.0%
Zr	0.0-10.0%
W	0.0-20.0%
Re	0.0-45.0%
Al	0.0-5.0%

(continued)

Cr	0.0-5.0%
V	0.0-10.0%
Nb	0.0-2.0%
Ta	0.0-2.0%
B	0.5-4.0%
Si	1.0-4.5%

and one or more of Ti, Zr, Hf or Al in an amount of 0.3-10% and the balance is 50-98.5% Mo apart from impurities wherein % is weight %, the molybdenum alloy optionally comprising up to 2.5 volume % carbides.

2. A molybdenum alloy as claimed in claim 1 having a resistance to oxidation such that said alloys lose less than about 0.025 cm (0.01") of thickness from each surface of said alloy when heated to 1090°C (2000°F) in air for two hours.

3. A molybdenum alloy as claimed in either one of Claims 1 and 2 having a yield strength of greater than 60 ksi at 1090°C (2000°F) ; wherein said yield strength is measured on a round specimen formulated and tested per ASTM E21-79.

4. A molybdenum alloy as claimed in any one of Claims 1 to 3 comprising at least one element in the stated quantity selected from the group consisting of:

C	0.01-1.0%
Ti	0.1-15.0%
Hf	0.1-10.0%
Zr	0.1-10.0%
W	0.1-20.0%
Re	0.1-45.0%
Al	0.1-5.0%
Cr	0.1-5.0%
V	0.1-10.0%
Nb	0.1-2.0%
Ta	0.1-2.0%

wherein % is weight %.

5. A molybdenum alloy as claimed in any one of Claims 1 to 4 comprising at least one element selected from the group consisting of:

C	0.03-0.3%
Ti	0.3-10.0%
Hf	0.3-3.0%
Zr	0.3-3.0%
W	0.3-3.0%
Re	2.0-10.0%
Al	0.5-2.0%
Cr	0.5-2.0%
V	0.3-5.0%
Nb	0.3-1.0%
Ta	0.3-1.0%

wherein % is weight %.

6. A molybdenum alloy as claimed in any one of Claims 1 to 5 having a resistance to oxidation such that said alloys lose less than about 0.025 cm (0.01") of thickness from each surface of said alloy when heated to 1370°C (2500°F) in air for two hours.

7. An alloy as claimed in any one of Claims 1 to 6 comprising at least 89 weight % Mo.

8. An alloy as claimed in any one of Claims 1 to 7, wherein said intermetallic phases comprise 10 to 70 volume % molybdenum borosilicide, less than 20 volume % molybdenum boride and less than 20 volume % molybdenum silicide, are discontinuous and dispersed in said matrix of body centered cubic molybdenum.

9. An alloy as claimed in any one of Claims 1 to 8, wherein said alloy comprises 2% silicon and 1% boron and said intermetallic phases occupy 30 to 35 volume %.

10. An alloy as claimed in any one of Claims 1 to 9 in the form of a jet engine part.

11. A method for enhancing the oxidation resistance of a molybdenum alloy comprising the step of adding silicon and boron to a molybdenum composition comprised of more than 50 weight % molybdenum; wherein said step of adding comprises adding silicon and boron to a melt comprising molybdenum followed by rapid solidification; and further comprising the step of consolidating the rapidly solidified alloy to form an alloy in which there is a matrix of body centred cubic molybdenum surrounding discrete particles of intermetallic phase; and further wherein said silicon and boron are added in amounts such that the molybdenum alloy having enhanced oxidation resistance that results from said step of adding, is an alloy as claimed in any one of claims 1 to 9.

12. A method as claimed in Claim 11 wherein said step of adding comprises adding silicon and boron to a melt comprising molybdenum followed by rapid solidification of the resulting mixture into a fine powder; and further comprising consolidation of said powder by a method selected from the group consisting of extrusion, hot pressing, hot vacuum compaction, hot isostatic pressing, and sintering.

13. A method as claimed in either one of Claims 11 and 12 wherein said metal of the molybdenum alloy consists essentially of molybdenum and at least one element in the stated quantity selected from the group consisting of:

C	0.1-1.0%
Ti	0.1-15.0%
Hf	0.1-10.0%
Zr	0.1-10.0%
W	0.1-20.0%
Re	0.1-45.0%
Al	0.1-5.0%
Cr	0.1-5.0%
V	0.1-10.0%
Nb	0.1-2.0%
Ta	0.1-2.0%

wherein % is weight %.

14. A method of making a molybdenum alloy of Claim 1 comprising the steps of forming a melt consisting of:

C	0.0-1.0%
Ti	0.0-15.0%
Hf	0.0-10.0%
Zr	0.0-10.0%
W	0.0-20.0%
Re	0.0-45.0%
Al	0.0-5.0%
Cr	0.0-5.0%

(continued)

V	0.0-10.0%
Nb	0.0-2.0%
Ta	0.0-2.0%
B	0.5-4.0%
Si	1.0-4.5%

and one or more of Ti, Zr, Hf or Al in an amount of 0.3-10% and the balance is 50-98.5% Mo apart from impurities wherein % is weight %, 2.5 rapidly solidifying said melt to form a rapidly solidified material; and consolidating said rapidly solidified material to form an alloy as defined in any one of claims 1-9 in which there is a matrix of body centred cubic molybdenum surrcunding discrete particles of intermetallic phase.

15. A method as claimed in Claim 14 wherein said alloy is made by consolidating a rapidly solidified powder at a temperature below the melting temperature of molybdenum.

16. A method as claimed in either one of Claims 14 and 15 wherein said step of consolidating is selected from the group consisting of extrusion, hot pressing, hot vacuum compaction, hot isostatic pressing, and sintering.

Patentansprüche

1. Eine Molybdänlegierung, bestehend aus einer Matrix von körperzentriertem, kubischem Molybdän und dispergierten, intermetallischen Phasen, die 10 bis 70 Vol.-% Molybdänborosilizit, weniger als 20 Vol.-% Molybdänborid und weniger als 20 Vol.-% Molybdänsilizit enthalten, und bestehend aus:

C	0,0-1,0 %
Ti	0,0-15,0 %
Hf	0,0-10,0 %
Zr	0,0-10,0 %
W	0,0-20,0 %
Re	0,0-45,0 %
Al	0,0-5,0 %
Cr	0,0-5,0 %
V	0,0-10,0 %
Nb	0,0-2,0 %
Ta	0,0-2,0 %
B	0,5-4,0 %
Si	1,0-4,5 %

und wobei eines oder mehrere von Ti, Zr, Hf oder Al in einer Menge von 0,3-10 % und der Rest 50-98,5 % Mo, abgesehen von Fremdstoffen, ist, wobei % Gew.-% ist, wobei die Molybdänlegierung wahlweise bis zu 2,5 Vol.-% Carbide enthält.

2. Molybdänlegierung gemäß Anspruch 1, die eine Oxidationsbeständigkeit hat, so daß die Legierungen weniger als etwa 0,025 cm (0,01") an Dicke von jeder Oberfläche der Legierung verlieren, wenn diese für zwei Stunden auf 1090 °C (2000 °F) an der Luft erhitzt wird.

3. Molybdänlegierung, gemäß einem der Ansprüche 1 und 2, die eine Dehngrenze von mehr als 60 ksi bei 1090 °C (2000 °F) hat; wobei die Dehngrenze auf einem runden Probekörper, per ASTM E21-79 formuliert und getestet, gemessen wurde.

4. Molybdänlegierung gemäß einem der Ansprüche 1 bis 3, die mindestens ein Element in der angegebenen Quantität enthält, das aus der Gruppe ausgewählt ist, die aus folgendem besteht:

C	0,01-1,0 %
Ti	0,1-15,0 %
Hf	0,1-10,0 %
Zr	0,1-10,0 %
W	0,1-20,0 %
Re	0,1-45,0 %
Al	0,1-5,0 %
Cr	0,1-5,0 %
V	0,1-10,0 %
Nb	0,1-2,0 %
Ta	0,1-2,0 %

wobei % Gew.-% ist.

5. Molybdänlegierung gemäß einem der Ansprüche 1 bis 4, die mindestens ein Element enthält, das aus der Gruppe ausgewählt ist, die aus folgendem besteht:

C	0,03-0,3 %
Ti	0,3-10,0 %
Hf	0,3-3,0 %
Zr	0,3-3,0 %
W	0,3-3,0 %
Re	2,0-10,0 %
Al	0,5-2,0 %
Cr	0,5-2,0 %
V	0,3-5,0 %
Nb	0,3-1,0 %
Ta	0,3-1,0 %

wobei % Gew.-% ist.

6. Molybdänlegierung gemäß einem der Ansprüche 1 bis 5, die eine Oxidationbeständigkeit hat, so daß die Legierungen weniger als etwa 0,025 cm (0,01") an Dicke von jeder Oberfläche der Legierung verlieren, wenn diese für zwei Stunden auf 1370 °C (2500 °F) an der Luft erhitzt wird.

7. Legierung gemäß einem der Ansprüche 1 bis 6, die mindestens 89 Gew.-% Mo enthält.

8. Legierung gemäß einem der Ansprüche 1 bis 7, wobei die intermetallischen Phasen 10 bis 70 Vol.-% Molybdänborosilizit, weniger als 20 Vol.-% Molybdänborid und weniger als 20 Vol.-% Molybdänsilizit enthalten, diskontinuierlich sind und in der Matrix des körperzentrierten, kubischen Molybdäns dispergiert werden.

9. Legierung gemäß einem der Ansprüche 1 bis 8, wobei die Legierung 2 % Silikon und 1 % Bor enthält und die intermetallischen Phasen 30 bis 35 Vol.-% beanspruchen.

10. Legierung gemäß einem der Ansprüche 1 bis 9 in der Form eines Düsentriebwerk-Teils.

11. Verfahren zur Vergrößerung der Oxidationbeständigkeit einer Molybdänlegierung, bestehend aus dem Schritt des Zugebens von Silikon und Bor zu einer Molybdänzusammensetzung, die aus mehr als 50 Gew.-% Molybdän besteht; wobei der Schritt des Zugebens das Zugeben von Silikon und Bor zu einer Schmelze, bestehend aus Molybdän, gefolgt von rapider Verhärtung, beinhaltet; und ferner bestehend aus dem Schritt des Verfestigens der rapid verhärteten Legierung, um eine Legierung zu bilden, in der eine Matrix aus körperzentriertem, kubischem Molybdän vorhanden ist, die diskrete Partikel intermetallischer Phasen umgibt; und ferner wobei Silikon und Bor in Mengen zugegeben werden, so daß die Molybdänlegierung, die eine verbesserte Oxidationsbeständigkeit aufweist, die aus dem Schritt des Zugebens resultiert, eine Legierung gemäß einem der Ansprüche 1 bis 9 ist.

12. Verfahren gemäß Anspruch 11, wobei der Schritt des Zugebens, daß Zugeben von Silikon und Bor zu einer Schmelze, bestehend aus Molybdän, beinhaltet, gefolgt von rapider Verhärtung der resultierenden Mischung zu einem feinen Puder; und ferner bestehend aus der Verfestigung des Puders mittels eines Verfahrens, das aus der Gruppe, die aus Extrudieren, Heißpressen, Heißvakuumverdichten, heißisostatischem Pressen und Sintern besteht, ausgewählt wird.

13. Verfahren gemäß einem der Ansprüche 11 und 12, wobei das Metall der Molybdänlegierung im wesentlichen aus Molybdän und mindestens einem Element in der angegebenen Quantität besteht, das aus der Gruppe ausgewählt wird, die aus folgendem besteht:

C	0,1-1,0 %
Ti	0,1-15,0 %
Hf	0,1-10,0 %
Zr	0,1-10,0 %
W	0,1-20,0 %
Re	0,1-45,0 %
Al	0,1-5,0 %
Cr	0,1-5,0 %
V	0,1-10,0 %
Nb	0,1-2,0 %
Ta	0.1-2.0 %

wobei % Gew.-% ist.

14. Verfahren zur Herstellung einer Molybdänlegierung gemäß Anspruch 1, das die Schritte zur Formung einer Schmelze beinhaltet, bestehend aus:

C	0,0-1,0 %
Ti	0,0-15,0 %
Hf	0,0-10,0 %
Zr	0,0-10,0 %
W	0,0-20,0 %
Re	0,0-45,0 %
Al	0,0-5,0 %
Cr	0,0-5,0 %
V	0,0-10,0 %
Nb	0,0-2,0 %
Ta	0,0-2,0 %
B	0,5-4,0 %
Si	1,0-4,5 %

und wobei eines oder mehrere von Ti, Zr, Hf oder Al in einer Menge von 0,3-10 % und der Rest 50-98,5 % Mo, abgesehen von Fremdstoffen, ist, wobei % Gew.-% ist, dem rapiden Verhärten lassen der Schmelze, um ein rapide verhärtetes Material zu formen; und, dem Verfestigen lassen des rapide verhärteten Materials, um eine Legierung gemäß einem der Ansprüche 1-9 zu formen, die aus einer Matrix von körperzentriertem, kubischem Molybdän, welches diskrete Partikel intermetallischer Phasen umgibt, besteht.

15. Verfahren gemäß Anspruch 14, wobei die Legierung durch Verfestigen eines rapide verhärteten Pulvers, bei einer Temperatur, die unter der Schmelztemperatur von Molybdän liegt, hergestellt wird.

16. Verfahren gemäß einem der Ansprüche 14 und 15, wobei der Schritt des Verfestigens aus der Gruppe ausgewählt wird, die aus Extrudieren, Heißpressen, Heißvakuumverdichten, heißisostatischem Pressen und Sintern besteht.

Revendications

1. Un alliage de molybdène composé d'une matrice de molybdène cubique à corps centré et de phases intermétalliques dispersées comprenant de 10 à 70 % en volume de borosiliciure de molybdène, moins de 20 % en volume de borure de molybdène et moins de 20 % en volume de siliciure de molybdène et constitué de :

C	0,0 à 1,0 %
Ti	0,0 à 15,0 %
Hf	0,0 à 10,0 %
Zr	0,0 à 10,0 %
W	0,0 à 20,0 %
Re	0,0 à 45,0 %
Al	0,0 à 5,0 %
Cr	0,0 à 5,0 %
V	0,0 à 10,0%
Nb	0,0 à 2,0 %
Ta	0,0 à 2,0 %
B	0,5 à 4,0 %
Si	1,0 à 4,5 %

un ou plusieurs composants parmi Ti, Zr, Hf et Al étant présents dans une quantité allant de 0,3 à 10 % et la proportion de Mo, impuretés mises à part, allant de 50 à 98,5 %, dans lequel % est % en poids, l'alliage de molybdène comprenant de façon optionnelle jusqu'à 2,5 % en volume de carbures.

2. Un alliage de molybdène tel que revendiqué dans la revendication 1 ayant une résistance à l'oxydation telle que chaque surface desdits alliages perd moins de 0,025 cm (0,01") d'épaisseur environ lorsque ledit alliage est chauffé à 1 090 °C (2 000 °F) dans de l'air pendant deux heures.

3. Un alliage de molybdène tel que revendiqué dans l'une ou l'autre des revendications 1 et 2 ayant une limite élastique supérieure à 60 ksi à 1 090 °C (2 000 °F) ; dans lequel ladite limite élastique est mesurée sur un spécimen rond formulé et testé suivant l'ASTM E21-79.

4. Un alliage de molybdène tel que revendiqué dans une quelconque des revendications 1 à 3 comprenant au moins un élément dans la quantité spécifiée sélectionné dans le groupe constitué de :

C	0,01 à 1,0 %
Ti	0,1 à 15,0 %
Hf	0,1 à 10,0 %
Zr	0,1 à 10,0 %
W	0,1 à 20,0 %
Re	0,1 à 45,0 %
Al	0,1 à 5,0 %
Cr	0,1 à 5,0 %
V	0,1 à 10,0 %
Nb	0,1 à 2,0 %
Ta	0,1 à 2,0 %

dans lequel % est % en poids.

5. Un alliage de molybdène tel que revendiqué dans une quelconque des revendications 1 à 4 comprenant au moins un élément sélectionné dans le groupe constitué de :

C	0,03 à 0,3 %
Ti	0,3 à 10,0 %

(suite)

Hf	0,3 à 3,0 %
Zr	0,3 à 3,0 %
W	0,3 à 3,0 %
Re	2,0 à 10,0 %
Al	0,5 à 2,0 %
Cr	0,5 à 2,0 %
V	0,3 à 5,0 %
Nb	0,3 à 1,0 %
Ta	0,3 à 1,0 %

dans lequel % est % en poids.

6. Un alliage de molybdène tel que revendiqué dans une quelconque des revendications 1 à 5 ayant une résistance à l'oxydation telle que chaque surface desdits alliages perd moins de 0,025 cm (0,01") d'épaisseur environ lorsque ledit alliage est chauffé à 1 370 °C (2 500 °F) dans de l'air pendant deux heures.

7. Un alliage tel que revendiqué dans une quelconque des revendications 1 à 6 comprenant au moins 89 % en poids de Mo.

8. Un alliage tel que revendiqué dans une quelconque des revendications 1 à 7, dans lequel lesdites phases intermétalliques comprennent de 10 à 70 % en volume de borosiliciure de molybdène, moins de 20 % en volume de borure de molybdène et moins de 20 % en volume de siliciure de molybdène, sont discontinues et sont dispersées dans ladite matrice de molybdène cubique à corps centré.

9. Un alliage tel que revendiqué dans une quelconque des revendications 1 à 8, dans lequel ledit alliage comprend 2 % de silicium et 1 % de bore et lesdites phases intermétalliques occupent de 30 à 35 % en volume.

10. Un alliage tel que revendiqué dans une quelconque des revendications 1 à 9 sous la forme d'une pièce de moteur à réaction.

11. Un procédé destiné à accroître la résistance à l'oxydation d'un alliage de molybdène comprenant l'étape consistant à ajouter du silicium et du bore à une composition au molybdène qui comprend plus de 50 % en poids de molybdène ; dans lequel ladite étape d'ajout comprend l'ajout de silicium et de bore à un bain de fusion comprenant du molybdène suivi d'une solidification rapide ; et comprenant en outre l'étape consistant à consolider l'alliage rapidement solidifié afin de former un alliage dans lequel une matrice de molybdène cubique à corps centré entoure des particules discrètes de phase intermétallique ; et dans lequel, en outre, ledit silicium et ledit bore sont ajoutés en quantités telles que l'alliage de molybdène ayant une résistance à l'oxydation accrue en résultat de ladite étape d'ajout est un alliage tel que revendiqué dans une quelconque des revendications 1 à 9.

12. Un procédé tel que revendiqué dans la revendication 11 dans lequel ladite étape d'ajout comprend l'ajout de silicium et de bore à un bain de fusion comprenant du molybdène suivi de la solidification rapide du mélange résultant en une poudre fine ; et comprenant en outre la consolidation de ladite poudre par un procédé sélectionné dans le groupe constitué d'extrusion, de compression à chaud, de compactage sous vide à chaud, de compression isostatique à chaud et de frittage.

13. Un procédé tel que revendiqué dans l'une ou l'autre des revendications 11 et 12 dans lequel ledit métal de l'alliage de molybdène est constitué essentiellement de molybdène et d'au moins un élément dans la quantité spécifiée sélectionné dans le groupe constitué de :

C	0,1 à 1,0 %
Ti	0,1 à 15,0 %
Hf	0,1 à 10,0 %
Zr	0,1 à 10,0 %
W	0,1 à 20,0 %

(suite)

Re	0,1 à 45,0 %
Al	0,1 à 5,0 %
Cr	0,1 à 5,0 %
V	0,1 à 10,0 %
Nb	0,1 à 2,0 %
Ta	0,1 à 2,0 %

dans lequel % est % en poids.

14. Un procédé de fabrication d'un alliage de molybdène de la revendication 1 comprenant les étapes consistant à former un bain de fusion constitué de :

C	0,0 à 1,0 %
Ti	0,0 à 15,0 %
Hf	0,0 à 10,0 %
Zr	0,0 à 10,0 %
W	0,0 à 20,0 %
Re	0,0 à 45,0 %
Al	0,0 à 5,0 %
Cr	0,0 à 5,0 %
V	0,0 à 10,0 %
Nb	0,0 à 2,0 %
Ta	0,0 à 2,0 %
B	0,5 à 4,0 %
Si	1,0 à 4,5 %

un ou plusieurs composants parmi Ti, Zr, Hf et Al étant présents dans une quantité allant de 0,3 à 10 % et la proportion de Mo, impuretés mises à part, allant de 50 à 98,5 %, dans lequel % est % en poids ; à rapidement solidifier ledit bain de fusion afin de former une matière rapidement solidifiée ; et à consolider ladite matière rapidement solidifiée afin de former un alliage tel que défini dans une quelconque des revendications 1 à 9 dans lequel une matrice de molybdène cubique à corps centré entoure des particules discrètes de phase intermétallique.

15. Un procédé tel que revendiqué dans la revendication 14 dans lequel ledit alliage est fabriqué en consolidant une poudre rapidement solidifiée à une température en dessous de la température de fusion du molybdène.

16. Un procédé tel que revendiqué dans l'une ou l'autre des revendications 14 et 15 dans lequel ladite étape de consolidation est sélectionnée dans le groupe constitué d'extrusion, de compression à chaud, de compactage sous vide à chaud, de compression isostatique à chaud et de frittage.


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FIG. 1

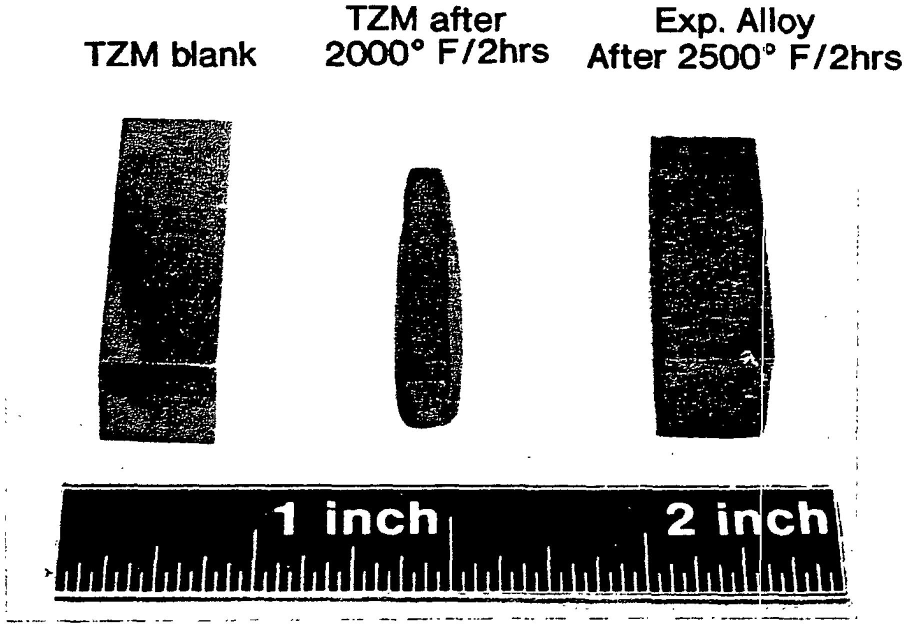
TZM blank
TZM after 2000° F/2hrs
Exp. Alloy After 2500° F/2hrs
1 inch
2 inch

FIG. 2